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Analytical Instrument Performance Criteria

International Standard Procedure for the Extraction of Metal Compounds Having Soluble Threshold Limit Values

Kevin Ashley, Column Editor

Reported on behalf of the International Organization for Standardization, Technical Committee 146 on Air Quality, Subcommittee 2 on Workplace Atmospheres, Working Group 2 on Inorganic Particulate Matter (ISO/TC 146/SC 2/WG 2)

The lack of guidance on sample treatment procedures for the measurement of soluble metal compounds in workplace air samples has been problematic for years. It is the intention of the present article to address this important issue by alerting the occupational and environmental health community of the existence of a newly promulgated "soluble" metals procedure, which has been published recently in an International Standard. The subject matter of this article may not appear to deal directly with "instrument performance criteria"; however, sample preparation methods for soluble metal compounds are design-based, and do indeed have a bearing on the subsequent instrumental analysis.

Several years ago, the issue of metals and solubility, as it pertains to the American Conference of Governmental Industrial Hygienists' (ACGIH®) Threshold Limit Values (TLVs®), was discussed extensively by Fairfax and Blotzer.(1) The matter is revisited here in view of the recent final approval of an International Standard, developed by the International Organization for Standardization (ISO), which describes methods for extracting metals and metalloids from workplace air samples for their subsequent determination.(2) One of the procedures described in this standard, Annex B of ISO 15202-2,(3) addresses the extraction of soluble metals and metalloids for their measurement using inductively coupled plasma atomic emission spectrometry (ICP-AES). One aim of the present article is to describe the salient features of the newly promulgated International Standard procedure for soluble metals and metalloids.[1] Additionally, other pertinent publications, standards, and background information, considered during the development of Annex B of this International Standard, are discussed.

Metals and metalloids having soluble TLVs, as published in the 2001 ACGIH TLV Handbook,(4) are listed in Table I. For most of these elements, the TLVs for the soluble compounds are lower than for the corresponding insoluble forms (Al, Ag, Cr^{VI}, Mo, Ni, Pt, Rh, W), while TLVs for soluble and insoluble compounds (Ba, Fe, Tl) of the remaining elements are the same.(4) It is not within the scope of this column to discuss issues concerning relative toxicities and related manifestations of the elemental species and their TLVs for soluble and insoluble forms, as these matters have been discussed aptly by Fairfax and Blotzer in their article.(1) Rather, the intention here is to present the important technical features of the soluble sample preparation procedures as described in the new ISO standard,(3) with rationale given for the chosen methods.

In their paper, which was written on behalf of the ACGIH Chemical Substances TLV Committee (Dusts and Inorganics Subcommittee), Fairfax and Blotzer arrived at several conclusions and questions regarding soluble TLVs for metallic elements.(1) These authors noted that background information supporting the soluble TLVs did not prescribe specific sample preparation procedures for the determination of soluble metals and metalloids. The lack of a standard soluble sample preparation method for industrial hygiene samples has led to significantly disparate results obtained in different laboratories. Such conflicting data have resulted largely from intractable measurement uncertainties, owing to numerous uncontrolled variables resulting from the lack of standardization. Notably, a consistent definition of "soluble," as it pertains to metallic elements, has been largely lacking. Various procedures for the extraction of soluble metals and metalloids have been used for years, based on different operational definitions of solubility. A goal of ISO/TC 146/SC 2/WG 2 was to standardize extraction procedures for "soluble" metal compounds by offering an operational definition in terms of a soluble sample preparation method for metallic elements in industrial hygiene measurements.

Operational Definition of "Soluble"

What is meant by "soluble" depends on the operational definition employed for the extraction conditions desired by the investigator. The term "solubility," as used by analytical chemists, ordinarily

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[1] It is noted that other annexes within the International Standard, which are not discussed here, describe procedures for the extraction of total recoverable metals.

TABLE I
Metallic elements for which soluble compounds have been assigned TLVs.(4)

Element and soluble compounds thereof	TLV, Time-Weighted Average (mg/m^3)
Aluminum—Soluble salts, as Al	2
Barium—Soluble compounds, as Ba	0.5
Chromium—Water-soluble Cr^{VI} compounds	0.05
Iron—Soluble salts, as Fe	1
Molybdenum—Soluble compounds, as Mo	0.5
Nickel—Soluble compounds, as Ni	0.1
Platinum—Soluble salts, as Pt	0.002
Rhodium—Soluble compounds, as Rh	0.01
Silver—Soluble compounds, as Ag	0.01
Thallium—Soluble compounds, as Tl	0.1
Tungsten—Soluble compounds, as W	1
Uranium—Soluble compounds, as U	0.2

pertains to the dissolution of a material in pure water.(5) Other pertinent references sustain the notion that solubility, regarding metals and their compounds, is generally identified in terms of their solubility in water.(6–8) However, this characterization does not accurately reflect the solubility of metals and their compounds in biological fluids. Fairfax and Blotzer argued that solubility in body fluids should be considered in the development of a new definition for soluble TLVs.(1) However, since different body fluids have different solubility characteristics (e.g., pH, salts, polypeptides), such an operative, uniform definition for "bioavailable" cannot realistically be determined. Indeed, what is meant by "bioavailability" has been debated nationally and internationally for years, and it was not deemed practicable nor defensible to attempt to operationally define solubility based on biochemical arguments. Hence, it was decided by consensus within the ISO working group (ISO/TC 146/SC 2/WG 2) to describe a soluble metals procedure in terms of strictly chemical, and not biological or biochemical, criteria.

With regard to analytical methods for the extraction of soluble metals and their compounds, Fairfax and Blotzer suggested that the extraction media, temperature, and volume should be consistent among all laboratories.(1) It is necessary to delineate these experimental criteria in order to offer an operational definition of "soluble," and to fully standardize the extraction procedure for soluble metal species. Moreover, the apparatus used, as well as chemical compatibility issues, must be amply described. Matters outside of the laboratory's control, notably sampling, cannot always be adequately influenced; however, recommendations as to sampling media, sample handling, and transport requirements should be provided to the field industrial hygienist.

A number of measurement methods for soluble metal compounds in occupational hygiene samples have been published.(9–12) Additionally, guidance on sample preparation methods for soluble metals and metalloids in workplace air has been promulgated very recently in a European Standard.(13) In these published methods and guidelines,(9–13) two methodologies are generally favored for the extraction of "soluble" metal species: (1) extraction in pure water, or (2) extraction in diluted (~0.1 M) hydrochloric acid (HCl). In the European Standard,(13) both strategies are given as options for the dissolution of "soluble" metals in workplace air samples. Extraction of metals and metalloids in water is meant to reflect the chemical definition of "soluble" (as mentioned above), while extraction in diluted HCl is designed to mimic the dissolution of "soluble" metal compounds in stomach acid, which is highly acidic (pH ≈1). A temperature of 37°C is recommended because it is normal body temperature.

In a recent paper,(14) Hahn argued for the establishment of 0.1 M HCl in an operational definition for soluble metals in occupational hygiene samples, and also specified mechanical agitation at 37°C for two hours prior to sample analysis. An exception is made for thallium, which can form insoluble thallium chloride (TlCl), in which case HCl is replaced by diluted nitric acid (HNO_3). The German extraction method for several soluble metal species(12) is consistent with the strategy outlined by Hahn.(14) However, in standard methods promulgated by the USA,(9) the United Kingdom,(10) and France,(11) deionized water is the solvent chosen in the operational definition of "soluble" for numerous metallic elements in workplace air samples. An exception to extraction in water is made for nickel,(10) where an ammonium citrate solution is specified as the leachate for soluble compounds of this element. Ammonium citrate provides buffering and chelating properties that are desirable for leaching soluble nickel compounds.(10)

Besides workplace air or other environmental samples, an operational definition of "soluble" metal species for consumer products such as toys, paper products, and paints may also be considered.(15–17) Examples of standard procedures for the extraction of metal compounds from consumer products are based on sample treatments in 0.07–0.14 M HCl (depending on the sample) for an hour at either 37°C(15) or room temperature.(16) The American Society for Testing and Materials' (ASTM) procedure(15) is meant to provide an estimate of the bioavailability of several metals in art materials.

ISO Procedure for Soluble Metals and Metalloids

The ISO working group responsible for the development of ISO 15202-2, ISO/TC 146/SC 2/WG 2, began its task in September 1995, not long after the publication of the Fairfax and Blotzer

TABLE II
"Participating Member"* countries of ISO/TC 146/SC 2 (during the period of development of ISO 15202-2 [1996–2000]).

Belgium	Korea	Turkey
Germany	Netherlands	United Kingdom
India	Poland	United States
Italy	Spain	
Japan	Sweden	

*"Participating," or P-Member, countries are those nations able to vote on Draft International Standards, and therefore, may provide comments on the technical content of the documents during voting. "Observing," or O-Member, nations (not listed) may also offer comments, and can participate in the development of ISO standards. However, in the formal ISO voting process, O-Member nations can only vote on Final Draft International Standards, at which stage exclusively editorial, and non-technical, changes may be made.

article.(1) Shown in Table II is a list of countries that participated in voting on the technical content of the draft international standard when it was circulated for balloting, during the period 1996–2000.

Because of the various operational definitions for "soluble" metal compounds, a significant challenge was presented to the ISO working group responsible for the development of an international standard method to describe a procedure for extracting soluble metals and metalloids for subsequent atomic spectrometric measurement. Essentially, two choices were available, based on the standard methods previously mentioned above: (1) extraction in pure water, or (2) extraction in a dilute hydrochloric acid solution. It was decided by consensus of ISO delegates present at the earlier working group meetings to follow the former course, where solubility of metal compounds in occupational hygiene samples is defined in chemical terms. This decision was upheld during the later international voting process, which involved those countries listed in Table II. Nevertheless, text within the International Standard(3) states that individual countries may specify alternative procedures for the measurement of soluble metal species in workplace air samples. This, then, permits the option of using other extraction media such as dilute HCl.

The ISO procedure for soluble metals and metalloids assumes that samples were collected using the new International Standard for the collection of workplace air samples for subsequent multielement analysis, ISO 15202-1.(18) However, the choice of filter material used for the collection of samples targeted for the "soluble" metals procedure is important. Annex A of ISO 15202-1(18) and Annex B of ISO 15202-2(3) provide useful guidance on this subject. To wit, the filter medium used must not react with the airborne particulate collected by the sampler so as to change the chemical form of the sample. In particular, this can result if a soluble compound reacts with the filter material or a contaminant therein to produce an insoluble or less soluble compound. An example of this problem has been observed with silver, wherein a soluble silver compound, $AgNO_3$, reacted with chloride in mixed cellulose ester (MCE) filters to form AgCl, which is much less soluble in water.(19) Thus, low recoveries of "soluble" silver resulted, and it was necessary to choose an alternative filter medium, such as polytetrafluoroethylene (PTFE). Another problem can be seen with soluble forms of Cr^{VI}, which can react with the filter medium to form insoluble compounds and/or undergo reduction to Cr^{III}, and therefore be lost to analysis. Hence, chemical compatibility issues should be investigated prior to obtaining samples for "soluble" extraction procedures.

The sample dissolution method for soluble metal compounds is design-based; that is, the species measured is/are essentially defined by the specific leach solution and conditions used during sample preparation. Besides solubility in water, factors such as particle size, solute/solvent ratio, and the presence of other contaminants in the collected sample can influence the final analytical result. Thus, the sample extraction procedure, by definition, provides the desired analytical data.(3) If the dissolution procedure uses a solvent other than water, obviously the solubility characteristics of the method will be quite different.

The "soluble" metals procedure described in ISO 15202-2(3) lists all of the elements in Table I except for Cr^{VI} and Fe. Nevertheless, the sample preparation protocol described in this International Standard is certainly applicable to these two elements as well, although extracted Cr^{VI} requires stabilization in slightly basic, not acidic, solution. The ISO "soluble" metals method(3) calls for treatment of collected workplace filter samples in 5 mL of deionized water (or ammonium citrate leach solution in the case of Ni), and mechanical agitation in a water bath at 37° ± 2°C for 60 min. Undissolved material is thereafter filtered from the sample solution using a suction filtration apparatus or a syringe filter. One must also ensure that the filtration materials being used are unreactive toward the soluble metal compounds of interest. After filtration, the sample solution is acidified with nitric acid in order to stabilize the dissolved metallic elements within the extracted sample. This test sample is then ready for analysis by ICP-AES. Of course, other analytical techniques, e.g., atomic absorption spectrometry(20,21) or electrochemical analysis,(21,22) can be used as analytically equivalent alternatives.

Summary

With the promulgation of ISO 15202-2, many of the questions raised in the article by Fairfax and Blotzer(1) have been answered. The extraction medium and experimental conditions for the dissolution of "soluble" metal compounds have now been specified in a new International Standard procedure. Industrial hygienists and other professionals in the occupational and environmental health arena should be aware of the portion of this new standard that describes sample preparation procedures for soluble metal compounds. If the field industrial hygienist wishes to sample for soluble metals, guidance is now provided by this new

ISO standard for proper filter selection and subsequent sample preparation procedures. This standard has been sorely needed to ensure consistency and effectiveness in the extraction and analysis of soluble metal compounds from workplace air samples.

While this article has not discussed the analysis of "total" metals and metalloids, procedures for the determination of "total" metal content are also provided in the new International Standard.(2) The emphasis here has been on the description of the "soluble" procedure as this aspect was considered most important, due to the lack of standardized procedures for "soluble" metal compounds. It is hoped that through the use of ISO 15202-2, the occupational hygiene field will now be able to provide meaningful and consistent analytical results for soluble metal compounds in workplace air samples, and that significant disparities among laboratory results for such samples will be eliminated.

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